

Comment on “Sticking of Hydrogen on Supported and Suspended Graphene at Low Temperature”

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Abstract

The model of physisorption for hydrogen on suspended graphene proposed by Lepetit and Jackson [Phys. Rev. Lett. **107**, 236102 (2011)] is plagued by an infrared divergence. Fortunately, the radius of the supporting substrate holes provides a natural cutoff to regularize the model.

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Lepetit and Jackson (LJ) [1] propose a model for the physisorption of atomic hydrogen on suspended graphene via the emission of phonons (flexural ZA branch). In Fig. 2 of LJ, a phonon density of states (DOS) $\rho(\omega)$ is plotted that vanishes linearly with ω at zero frequency. This form for the density of states follows from having the graphene sheet under biaxial stress. LJ point out that in contrast to a constant DOS at zero frequency, a linear DOS eases a well-known divergence in the displacement autocorrelation function of the n th nearest neighbors $\langle (u_n - u_0)^2 \rangle$ in two dimensions [2].

In this Comment, the focus is on another divergence: a linear DOS, when combined with the frequency-dependent particle-phonon coupling V_c in their Eq. 1, gives a (log) divergent particle self-energy at second-order in V_c for zero temperature. This implies that without a low-frequency cut-off, the second-order shift in the binding energy in LJ's model of hydrogen on suspended graphene is infinite and the numerical calculation [1] can not be converged.

This divergence would also appear in a higher-order perturbative calculation of the sticking probability, as the sticking rate is proportional to the imaginary part of the self-energy. Drawing upon an analogy between low-energy physisorption and the spin-boson model [3], the coupling to the phonon bath in LJ is classified as subohmic with a frequency-dependent spectral density behaving as $J(\omega) \propto \omega^0$ at low frequencies. It is known [4] that such a case is plagued by an infrared divergence.

Neglecting contributions from the hydrogen continuum states, the second-order shift in the hydrogen binding energy $E_b^{(2)}$ from V_c is given by

$$E_b^{(2)} \approx \sum_{\mathbf{Q}} \frac{1}{\hbar\omega_{\mathbf{Q}}} |\langle b, 0 | V_c | b, \mathbf{Q} \rangle|^2 \quad (1)$$

where $|b, 0\rangle$ and $|b, \mathbf{Q}\rangle$ are eigenfunctions of the Hamiltonian [5] $H_s + H_b$, the former is the ground state and the latter state has an excitation of wave vector \mathbf{Q} in the bath.

In their Eq. 1, the summand of V_c is inversely proportional to $\sqrt{\omega_{\mathbf{Q}}}$. Hence in the continuum limit, $E_b^{(2)} \propto \int_0 d\omega \rho(\omega)/\omega^2$ which is log divergent for $\rho(\omega) \sim \omega$.

For a previous study of physisorption on graphite [5], $e_z(\mathbf{Q})$ tends to zero at the zone center and this divergence in the binding energy is avoided. The coupling to the bath in graphite would be classified as Ohmic with $J(\omega) \propto \omega$ at low frequencies. A superreflective transition for low-energy matter waves for such a system was recently predicted [6]; for energies below a critical value the sticking probability vanishes as a result of the orthogonality catastrophe.

The LJ model for suspended graphene can be regularized by introducing a low-frequency cutoff ω_c . There is an obvious choice for suspended graphene: the radius of the substrate holes, typically of the order of a few μm , gives rise to a fundamental vibrational resonance in the tens of MHz [7]. The exact value of the low-frequency cutoff is not essential, as relevant quantities computed to second-order have only logarithmic sensitivity to this cutoff.

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